

Room temperature p -induced surface ferromagnetism

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We prove a spontaneous magnetization of the oxygen-terminated ZnO (0001) surface by utilizing a multi-code, SIESTA and KKR, *first-principles* approach, involving both LSDA+U and self-interaction corrections (SIC) to treat electron correlation effects. Critical temperatures are estimated from Monte Carlo simulations, showing that at and above 300 K the surface is thermodynamically stable and ferromagnetic. The observed half-metallicity and long-range magnetic order originate from the presence of p -holes in the valence band of the oxide. The mechanism is universal in ionic oxides and points to a new route for the design of ferromagnetic low dimensional systems.

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Since the first report of magnetism in Co-doped ZnO [1] spontaneous magnetization persistent above room temperature (RT) has been found in a number of dilute magnetic oxides, even for materials containing no transition-metal impurities. The presence of ferromagnetism (FM) without magnetic elements has been revealed in thin films and nanoparticles of undoped HfO₂, ZnO, MgO, SnO₂, TiO₂ or SrTiO₃ [2, 3], among others. The measured FM in undoped, otherwise diamagnetic, bulk oxides presents several general and distinct characteristics such as a Curie temperature (T_C) substantially above room temperature, small coercive fields and a similar dependence of the coercive field and remanent magnetization on temperature [3]. This universality indicates a common origin. However, despite the intense research the physical origin of the magnetic ordering and, therefore, its control remains a controversial unresolved problem [4–6]. It was shown theoretically that localized holes in bulk oxides can lead to local moments and a half-metallic behavior [7]. However, a high T_C requires defect concentrations incompatible with the stability of the material. Furthermore, the necessary large strength and long-range of the defect-defect magnetic interaction is inconsistent with the actual localization of defect orbitals in ionic oxides [8].

In an alternative approach, which some of us proposed a few years ago, FM is induced at the surface due to its intrinsic characteristics: breakdown of symmetry, unsaturated bonds or uncompensated ionic charges [9, 10]. The physical mechanism underlying the spontaneous magnetization of the surface relies on the formation of holes at the top of the oxygen derived p -like minority valence band (VB) of the oxide. This mechanism is analogous to that responsible for cation vacancies [11] or acceptor doping [12] induced magnetism. Both, defects and surfaces impose boundary conditions, which give rise to the un-

compensated charges leading to magnetization. However, surface states, although confined to the topmost layers, are usually extended in two-dimensions [13] and, thus, the subtle interplay between localization and extended states, which is required for the moment formation and strong and long-range magnetic order, can be reached more easily at surfaces. In addition, there is growing experimental evidence that the FM signal is mostly concentrated in the near-surface region, grain boundaries or nanostructure interfaces [3, 14, 15].

Here we report a multi-code *first-principles* study of surface induced FM in ZnO, considered as the prototype of a high temperature (HT) FM oxide. We observe a spontaneous magnetization of the O-terminated ZnO (0001) surface when the oxygen atoms occupy the *fcc* three-fold coordinated sites. The magnetic interaction between spin moments is strong and the calculated Curie temperature is $\gtrsim 300$ K. The surface turns out to be thermodynamically stable in the range of oxygen pressures easily achieved experimentally. The underlying physical mechanism is universal in ionic oxides, although the onset of the spontaneous magnetization requires a critical number of p -holes, only achieved in specific surfaces.

In our calculations ZnO surfaces have been modeled by periodically repeated slabs separated by a vacuum region. To facilitate a more adequate treatment of electron correlations and p bands containing holes [8, 16], we have employed two approaches. First, the LSDA+U method, as implemented in the pseudopotential SIESTA code [17], known to well reproduce the groundstate of bulk ZnO [18], and second, the local self-interaction corrections (LSIC), as implemented in the multiple scattering theory, the LSIC-KKR code [19]. While the electronic structure and structural relaxations have been performed with SIESTA, the magnetic interactions for the relaxed

structures have been investigated with the LSIC-KKR code. In the latter, after determining the SIC ground-state, the system is mapped onto a Heisenberg Hamiltonian $H = -\sum_{ij} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j - \sum_i \Delta_i (e_i^z)^2$ by calculating the real space magnetic interaction parameters J_{ij} , where i and j stand for atomic sites, via the magnetic force theorem (MFT) [20]. Δ_i is the magnetic anisotropy energy at site i , and here has been treated as a parameter in the performed Monte Carlo (MC) simulations to estimate Curie temperatures [21].

Because of the symmetry of the ZnO crystal, Zn and O planes alternate along the [0001] direction and, due to the lack of inversion symmetry of the wurtzite structure, the polar (0001) and (000 $\bar{1}$) ZnO surfaces are inequivalent. Several positions of the surface oxygen atoms have been considered, including off-symmetric sites. We have found that the O-ZnO (000 $\bar{1}$) surface is stable and corresponds simply to the cleaved ZnO bulk crystal. The VB of surface oxygen is not entirely filled, hence surface layers are metallic and exhibit partly occupied flat surface states at the top of the VB [10, 18], although the number of holes is small, about 0.14 electrons. For the O-terminated (0001) surface, however, the most stable configuration turns out to be the one with oxygen in the three-fold *fcc* hollow site, as reported before [22]. This rearrangement of the top oxygen atom decreases the surface energy dramatically by ≈ 1 eV per O atom with respect to that of the cleaved cut-off crystal. The surface energy is even about 0.65 eV smaller than the formation energy of a Zn vacancy in bulk ZnO. The relaxed unit cell structure is illustrated in Fig. 1. The topmost oxygen atoms in both surfaces are

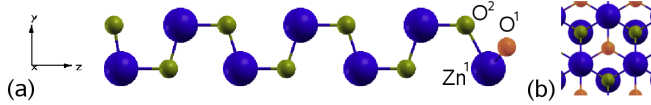


FIG. 1. (Color online) (a) The investigated ZnO slab unit cell (vacuum region not shown) in its groundstate structure after relaxation, with oxygen (small yellow and orange) and zinc (big blue) atoms. The (000 $\bar{1}$) surface is on the left end, the (0001) on the right. The latter is characterized by the topmost O atom in the three-fold coordinated hollow position, O^1 , and the Zn and O atom underneath, labelled Zn^1 and O^2 , respectively. (b) Topview of the (0001) surface.

three-fold coordinated, although the O-Zn distances are slightly compressed and relaxed in the (000 $\bar{1}$) and (0001) surfaces, respectively [18].

The layer resolved density of states (LDOS) corresponding to the (0001) surface is displayed in Fig. 2. The main features of the calculated LDOS reflect spin polarization and half-metallicity of the surface and the presence of the oxygen split-off band, with the Fermi level crossing the minority O band. The exchange splitting is large of about 1.5 eV and the narrowing of the minority bandwidth is particularly pronounced at the surface

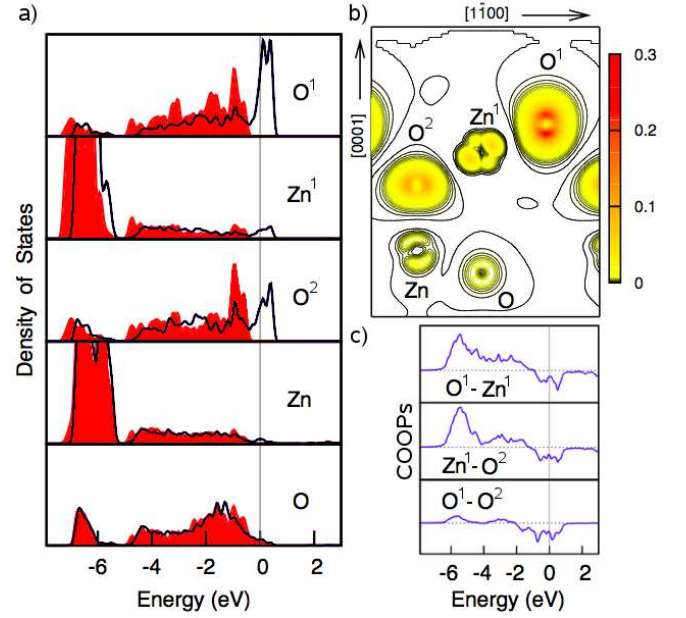


FIG. 2. (Color online) a) Spin resolved LDOS of the topmost layers of the O-ended (0001)-h surface. Red filled (black) values represent majority (minority) spin states. b) Spin density distribution of the (0001)-h surface. c) COOPs between the atoms in the first three layers. Energies are relative to E_F .

layer. The total magnetic moment (MM) is $\approx 1.5 \mu_B$ and the spin densities displayed in Fig. 2b confirm the surface localization of the magnetic moments.

The crystal orbital overlap populations (COOP) determine the wavefunction overlap of any two atoms and, therefore, their values can be related to their hybridization [23]. Thus, the COOP between the atoms close to the surface, shown in Fig. 2c, reveal a large hybridization between adjacent layers and evidence the extended character of states at the surface. Even the wavefunction overlap between O^1 and O^2 is noticeable, which is due to their short distance, 2.30 versus 3.25 Å for O atoms in the same plane.

The Mulliken charge differences and induced magnetic moments for the surface layers are given in Table I. It

TABLE I. Layer resolved Mulliken charge differences (in e) and magnetic moments (in μ_B) for the topmost layers of the (0001) surface. The layers are labeled according to Fig. 1.

	O^1	Zn^1	O^2
ΔQ	-0.38	-0.01	-0.19
MM (SIESTA)	0.94	0.01	0.53
MM (LSIC-KKR)	1.06	-0.06	0.42

shows that there is a charge rearrangement at the topmost atomic layers, more pronounced in the surface oxygen, which sustains more than 60 % of the induced *p*-holes. The orbital charge distribution is compatible with

the spatial symmetry and the larger number of holes localized in the p_z orbital [18]. The nominal Mulliken population for bulk ZnO is already reached three bilayers below the surface.

The surface induced p -holes give rise to an open-shell configuration of the oxygen which promotes the observed spontaneous spin-polarization of the surface, analogously to the well-known paramagnetism of the O_2 molecule. Therefore, the half-metallicity of the groundstate implies that surface magnetism is due to Hund's rule exchange, and electrons occupy orbitals in the open shell so as to maximize their total spin. The alignment of spins forming a symmetric spin state reduces the interaction energy. Therefore, whenever the energy gain from spin-splitting of the oxygen derived VB exceeds the energy loss in kinetic energy, it is advantageous for the system to spin-polarize. The COOPs displayed in Fig. 2c substantiate this conclusion. Since they represent the overlap of the wavefunction of the surface atoms, they clearly show that the states have itinerant character, and thus the delocalization necessary for the magnetic coupling.

As the coordination number is reduced at the surface and the narrow oxygen p band only partially filled, it is crucial to investigate also the degree of p electron localization and its importance for an adequate description of correlation effects. This has been accomplished with the LSIC-KKR method, for the relaxed surface [18]. The global SIC energy minimum has been found for the scenario where, in addition to all the Zn $3d$ electron states, all the majority, but no minority, p electrons of O^1 benefit from localization and hence self-interaction-correction. The resulting electronic structure [18] confirms that the exchange splitting is confined to the top-most oxygen sites (O^1 and O^2) and the top of the valence band, as shown in Fig. 2a. In Table I we show that the calculated MM on O^1 is increased due to the increased localization of the majority p band, causing an increased negative magnetization in the vicinity of the surface, with the half-metallicity preserved at the surface. The fact that the O^2 majority p states do not benefit from localization suggests that its MM is induced by O^1 through hybridization effects.

The exchange constants J_{ij} for the above SIC ground-state, calculated in the MFT approach, are presented in in Fig. 3. First, one sees that they are strongly ferromagnetic. Furthermore, the relevant contribution arises from interaction between O^1 - O^1 and O^1 - O^2 pairs. The reason for the very large nearest-neighbour (NN) coupling between O^1 and O^2 is the already mentioned close distance between these two atoms. The weak interaction between the O^2 atoms strengthens the assumption that the MM on them is induced by O^1 rather than being localized there. Figure 3 shows also that the J_{ij} 's have a similar behavior to such found for other half-metallic systems [24], i.e. they oscillate and decay relatively quickly. This means that the interaction is provided by the delo-

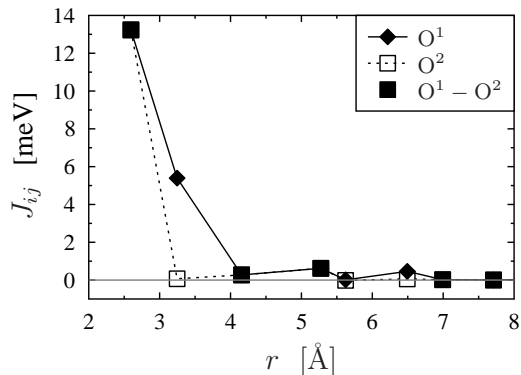


FIG. 3. J_{ij} of pairs containing O^1 (◆) or O^2 (□), respectively, depending on the distance. The full black squares (■) mark the J_{ij} between one O^1 and one O^2 atom.

calized electrons.

For the MC simulations the anisotropy Δ_i has been assumed to be the same at O^1 and O^2 , and treated as a parameter. Choosing $\Delta = 0.1, 0.3, 1.0$, and 3.0 eV the respective critical temperatures have come out to be larger than room temperature at $T_C = 302, 304, 320$, and 346 K, with an error of ≈ 6 K (15 K for $\Delta = 0.1$ eV due to a broad transition).

Owing to the large energy gain, the O-ZnO(0001) surface with O in the three-fold fcc hollow site, would be thermodynamically more stable than the O-ZnO(0001) cleaved surface, in the entire range of allowed O chemical potentials. Furthermore, the reduction of the surface energy is even sufficient to stabilize the full oxygen coverage of the (0001) surface for oxygen rich atmospheres [18]. In fact, several reports reveal the presence of oxygen atoms in ZnO(0001) surfaces [25], either in ordered structures [22, 26] or in extended O-terminated islands [27]. Therefore, the O-ZnO(0001) surface with O in the three-fold hollow site is a good candidate to explain the experimentally observed FM in thin layers and nanoparticles of ZnO. Consequently, the magnetic ordering is restricted to a small fraction of atoms located in the vicinity of the surface, which justifies the low magnetization measured [3, 14]. In addition, the likely presence of different polar and non-polar surfaces and probably adsorbates in the ZnO thin films and nanoparticles leads to a very complicated scenario, with magnetic and non-magnetic regions depending on the preparation conditions. This could explain the diversity of magnetic behaviors found experimentally. The possibility that boundaries are responsible for the FM of oxides is supported experimentally, since a surface contribution to the ferromagnetic hysteresis loops of the magnetization has been shown in a variety of common diamagnetic oxide crystals [3] and also a critical analysis of a large amount of published data for FM in Mn doped and pure ZnO strongly suggests that grain boundaries are the intrinsic origin for RT FM [15].

Since FM is predicted in polar surfaces it must be related to the stabilization mechanisms of those surfaces. Although usually their stabilization is explained in terms of ion removal or adsorption of charged molecules, it is still an open question and recently there has been evidence of electronic reconstruction and the formation of a 2D electron gas with exotic properties at the interfaces of ionic oxides [13, 28]. Therefore, spontaneous magnetization could be also a plausible general stabilization mechanism of polar ionic surfaces. The 2D electron gas induced by the uncompensated ionic charges at the surface can present a spin-polarized ground state.

In conclusion, by combining DFT-based and MC methods, we have predicted ferromagnetism at the oxygen terminated polar (0001) surface of ZnO with a T_C of $\gtrsim 300$ K. The spontaneous magnetization of the surface originates from the presence of p -holes in the minority valence band of the oxide, which renders a half-metallic surface. Spin-polarization is enhanced through the bandwidth reduction associated to the surface, which drives moment formation more efficiently. In addition, surface states, although confined to the topmost layers, are extended in two dimensions and thus the subtle interplay between localization and extended states required for the development of long-range magnetic order can be reached at the surface. The mechanism is universal in ionic oxides, provided that the localization of the p holes is strong enough for the formation of the MM. This novel two-dimensional magnetic state at the surface points to a new route for the design of ferromagnetic low dimensional systems.

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